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Alcoholic nanolime dispersion obtained by the insolubilisation-precipitation method and its application for the deacidification of ancient paper

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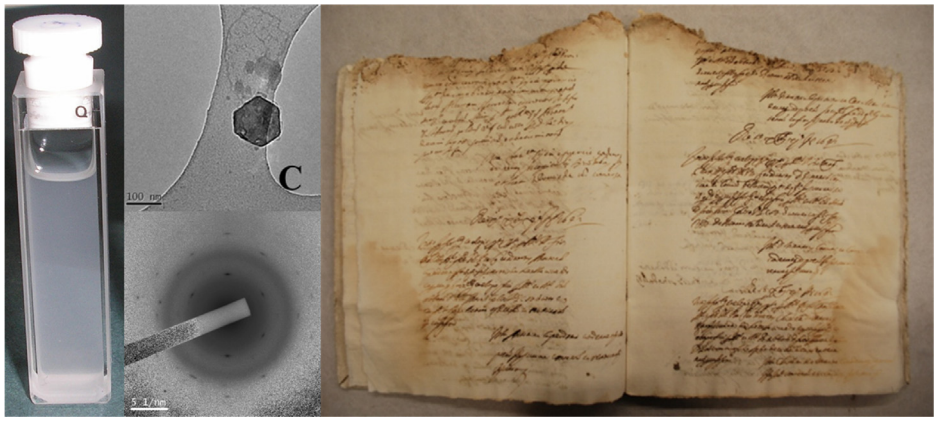
HIGHLIGHTS

- A new method for the calcium hydroxide nanoparticles preparation is proposed.
- A correlation between synthesis conditions and stability of the dispersion and particle size and morphology is demonstrated.
- The efficiency of nanolime dispersion in deacidification of an ancient manuscript is tested.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanolime dispersions for the deacidification of ancient paper constitute a valid alternative to the lime traditional ones. Their efficacy depends on particles size, polydispersity and agglomeration that can be controlled depending on the preparation method.

In this work, nanolime preparation by insolubilisation-precipitation method is reported. Nanoparticles dispersed in a water-isopropanol mixture were obtained without any manipulation of the dispersion. The stability of the dispersion together with particle size and morphology were found to be dependent on water to isopropanol molar ratio and on the synthesis temperature.

One of the dispersion was applied on a manuscript to assess its efficiency.

1. Introduction

In the last years, the use of $Ca(OH)_2$ nanoparticles in the field of cultural heritage has been extensively applied for its significant role proposed in the conservation treatments [1–4]. Many works have

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been published about the application of $Ca(OH)_2$ nanoparticles to restoration of frescoes [5,6], wall paintings [7,8], stones [9,10] as well as to the deacidification of paper and canvas [11,12].

Nanolime is an excellent deacidifying agent for cellulosic materials. It ensures a good physicochemical compatibility with the support, and after its transformation into calcium carbonate, it works very well as an alkaline reservoir and does not originate any undesirable side products [13,14]. One of the most famous and lucky examples is the Vasa warship [15,16] that represents a unique case in the study of ancient waterlogged wood and a challenge for finding new methods for artifacts conservation. Several authors have investigated and reported about the efficacy of nanolime on the deacidification of paper and canvas [12,17–19]. Some of them successfully used nanolime for the deacidification of paper containing iron gall ink. In fact the solvents, usually short chain alcohols mixtures, are highly compatible with components of the inks so that no bleeding are expected [18–20]. It has been already demonstrated that nanolime improved mechanical properties of paper and protected iron gall inked areas from discoloration during artificial aging [19].

It is well known that the efficiency of the treatment depends on nanolime morphology and size distribution, therefore the interest on different methodologies of synthesis arises from the fine control that can be achieved on particles size as well as on their morphology by choosing properly a synthetic strategy. Thus, the efficient methodology of synthesis requires a good mixing of the starting materials and chemical homogeneity of products. Several methodologies of synthesis of $Ca(OH)_2$ nanoparticles have been developed such as solvothermal [16,21], in homogeneous phase [12], micelles assisted [22], microemulsion water/oil assisted [23] or sol-gel [4,24]. However, most of these methods are very sophisticated, time consuming and expensive and a series of manipulations are necessary thus introducing impurities.

The aim of this study is to prepare nanolime dispersions whose particles have low polydispersity, low size and low agglomeration. At the same time, by simplifying the reaction conditions, a scale up of the synthesis can easily be foreseen.

In order to reach this goal, the insolubilisation-precipitation method was used. To our knowledge, this method has not been proposed in literature for $Ca(OH)_2$ nanoparticles synthesis [25]. It involves the preparation of an aqueous solution of calcium hydroxide at the solubility limit, to which a certain amount of 2-propanol is added thus causing the nanolime formation. The final hydroxide concentration is determined by the amount of saturated aqueous calcium hydroxide solution at a given temperature [26].

The main advantage of this method is due to the use of calcium hydroxide that, by alcohol addition, precipitates thus forming the nanolime dispersion in one step. Due to the low polarity of the solvent, the resulting alcoholic dispersion can be used on paper safer with respect to the saturated aqueous solution of calcium hydroxide.

The kinetic stability of the obtained dispersion was investigated by means of UV–Vis Spectroscopy. The particle size, polydispersity, composition and crystal structure were investigated by means of Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and Selected Area Electron Diffraction (SAED).

The nanolime dispersion having the best properties in terms of stability and particle size and polydispersity was used for the deacidification of an ancient manuscript of the *Archivio Storico Diocesano of Palermo*. This document belonged to the fund of the parish of *San Giovanni degli Eremiti (Palermo)*, later absorbed by the *Archivio Storico Diocesano of Palermo*, to which it still belongs. The archival document concerns the sentences dictated by the Grand Court of the Archbishop of Palermo in the years 1642 and 1643. It is divided into two parts. The first part is an index for easy reference: the list is in alphabetical order and it shows the names of those undergoing judgment, along with the page number. The second part of the book reports the actual judgments.

A preliminary diagnostic investigation on the document was performed before the treatment in order to get information on the pH of the paper, the nature of the ink and the conservation state of paper by using pHmetry, Raman and NMR Spectroscopy. The efficiency of the deacidification treatment was evaluated by the pH change.

2. Materials and methods

2.1. Sample preparation

2-propanol and calcium hydroxide were supplied by Merck, Darmstadt, Germany, and were used without any further purification. Water was purified by a Millipore Organex system ($R \geq 18\ M\Omega\ cm$) and de-carbonated by distillation on a substrate of potassium permanganate and sodium hydroxide (Sigma Aldrich).

The used experimental apparatus consists of a four necked flask connected to a six-bulb condenser, thermostated at 15 °C, to an optic-fibre thermometer, to a dropping funnel can and to a nitrogen tank to maintain the system under inert atmosphere. The flask is immersed in a bath of silicone oil at controlled temperature. The homogeneity of the dispersion is ensured by mechanical agitation via a magnetic stirrer.

Appropriate amounts of aqueous solutions of calcium hydroxide close to the solubility limit at 76 °C [26] were prepared by dissolving the appropriate quantity of the hydroxide in de-carbonated water. The solution concentration was 0.980 g/L.

In order to investigate the effect of temperature and of the amount of 2-propanol, the synthesis was carried out in the range 40–76 °C and of 20–90 vol.% of alcohol.

Dispersions A, B and C were prepared at 40, 60 and 76 °C and alcohol amount of 90 vol.%, by adding dropwise the alcohol to an aliquot of the calcium hydroxide aqueous solution. The latter temperature has been selected once known that the boiling temperature of the azeotrope water/2-propanol mixture, whose composition is 12 vol.% in water, is 80.4 °C [27].

Once established the best temperature to obtain a stable dispersion, in order to evaluate the effect of the alcohol amount on the kinetic stability of the suspensions and morphology of nanolime dispersions, two samples were prepared at 76 °C with different alcohol amount, 20 and 50 vol.% respectively, by adding dropwise the alcohol to aliquots of the calcium hydroxide aqueous solution. These two samples were called E and D.

The synthesis has been performed at atmospheric pressure and at controlled temperature as indicated above.

All prepared samples, whose composition is reported in Table 1, were analysed by turbidimetry and DLS. Samples E, D and C were investigated by TEM.

2.2. Sample characterization

The kinetic stability was evaluated via turbidimetric method [28] by computing the stability parameter $\xi = (A_t - A_\infty)/A_t$, as reported in the literature [12,29], where A_t is the absorbance value of the dispersion at a given time and A_∞ is the absorbance value at the end of the observations. UV–Vis spectra were recorded in the range 200–800 nm with resolution of 1.0 nm using a double beam Beckman DU-800 spectrophotometer. The absorbance values selected are those at 600 nm in correspondence of which the absorbance of species in suspension is negligible. ξ value ranges from 0 (complete sedimentation, unstable dispersion) to 1 (no settling of the particles, perfect kinetic stability of the dispersion).